Simple method and environmentally friendly ash content removal process from rice husk char using potassium carbonate solution

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Abstract
Carbonization of rice husk produces rice husk char with high ash content and silica. The main problem to obtain carbon from rice husk char is the release of silica. In this study, silica was released using potassium carbonate solution by reflux method. The purpose of this study was to determine the ratio of silica mole to potassium carbonate, reflux time and the calcination temperature of rice husk carbon.

The result of carbon activation was then characterized by ash content test, conductivity test, XRD, FTIR and SEM-EDX. In this study the ratio of potassium carbonate mole with silica content of 1: 3, reflux time for 2 hours and calcination temperature at 900^oC is known. Carbon was obtained in amorphous form with iodine number and methylene blue number of 556 mg/g and 66 mg/g respectively.

Keywords: Ash Content, Ash Removal, Rice Husk and Rice Husk Char.

Introduction

Rice husk is a source of carbon that is abundant, renewable and cheap. Rice husk is a by-product of rice milling. The main components of rice husks are cellulose (38%), hemi-cellulose (18%), lignin (22%) and SiO_2[1]. There are high carbon and silica compounds in rice husks and the carbonization process of rice husks produces composites containing carbon and silica.

The potential use of porous carbon materials in several fields has attracted researchers in recent years, especially in support of catalysts, battery electrodes, capacitors, gas storage and other engineering[2,3]. Porous carbon material contains sp^3 and sp^2 carbon fractions, the magnitude of each fraction depending on the preparation conditions and raw materials used. The existence of sp^2 carbon structures increase the use of wider carbon materials especially those related to electrical conductivity[4].

Wang et al[5] produced porous carbon from rice husks through a hydrothermal carbonization process and obtained carbon with coulombs capacity of about 137 $mA.g^{-1}$. The steps in the manufacturing process are pre-treatment with hydrochloric acid, hydrothermal carbonization in formic acid solution, calcination (carbonization continued) at 900°C and silica removal with ammonium hydrogen fluoride. Hydrothermal processes in formic acid solutions are subjected to hemicellulose and lignin dissolution causing a decrease in carbon yield and the need for special solution handling prior to discharge into the environment.

In addition to the removal of silica with hydrogen fluoride, silicone tetra fluoride is volatile, requiring special handling to prevent air pollution. Another, almost identical, method uses only hydrochloric acid and sodium hydroxide solution and its carbonization at a temperature of 700°C[6]. The results show carbon with the best conductivity is obtained using sodium hydroxide. This is because silica reacts with a solution of sodium hydroxide and more pores are formed on the carbon, although the carbon obtained is still low due to dissolution of hemicellulose and lignin.

Kennedy et al[7] produced carbon through two stages of carbonization, the first stage of carbonization at 400°C and then carbonized with adding phosphoric acid at higher temperatures (varied to 900°C). The study showed that the higher was the temperature, the higher was electrical conductivity. However, the increase was not satisfactory (up to order 10^{-3} $S.cm^{-1}$). This was due to the presence of insulating silica. The heat treatment study on cellulose showed the formation of carbon structure sp^2 (structures such as graphite) starting at 610°C with perfect temperature at 1200°C with electric conductivity ranging from the order of 10^{-2} - 10^{2} $S.cm^{-1}$. Thus the presence of silica in porous carbon greatly influences its conductivity.[8]

Rice husk can be used as base material to create conductive carbon through the formation of porous carbon. Some literature indicates that there is still a weakness in the manufacture of conductive carbon with low electrical conductivity, the process is still complicated and not environmentally friendly. This research will use low temperature carbonization followed by the process of removing ash content using potassium carbonate solution at varying concentrations.

The process using potassium carbonate solution produced silica and potassium carbonate solution can be recovered[9,10]. Silica can be used as a material for making various silica based materials such as silica gel, colloidal silica, catalyst support, zeolite, mesoporous silica and others. The activation process using potassium carbonate solution is a clean and simple production process.

Material and Methods

The char used rice husk (RH) from rice mills in Jatinangor Sumedang, West Java. 400 g sample of rice husk was carbonized in a closed electric furnace with carbonization temperature of 400°C for 4 hours. A K-type thermocouple and a digital temperature controller were used to set and control the sample temperature. The rice husk char were crushed until it passed the 100 mesh sieve and the ash content was measured.

Rice husk weighed as much as 50 g and alkali carbonate (Na or K) weighted accordingly to obtain a silica-alkali carbonate ratio of 1: 1, 1: 1.5, 1: 2 and 1: 3. Then 300 mL of distilled water was added to each composition, then refluxed for 1 hour. The residue (carbon) was separated and dried at 110°C for 4 hours. The residue was refluxed again with 1 M nitric acid for 2 hours. The residue was washed with distilled water until pH neutral and dried in an oven at 110°C and cooled.

The silica-free carbons containing the lowest ash content were calcined at a temperature of 500, 700 and 900°C for 2 hours under inert atmosphere of argon at a rate of 30 mL/min. Rice husk char and carbon were characterized by using X-ray Diffractometer (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM).

Results and Discussion

Varying the mole ratio of potassium carbonate to the silica content on charcoal was done to determine the best ratio for silica extraction to obtain pure carbon. The result can be seen in figure 1 which explains the ash content obtained for each ratio through the reflux method. Figure 1 clearly shows the decrease insilica content in rice husk charcoal by increasing the extraction ratio. Carbons having the lowest ash content were obtained from extraction with a 3:1 ratio of potassium carbonate to silica content for all extraction methods.

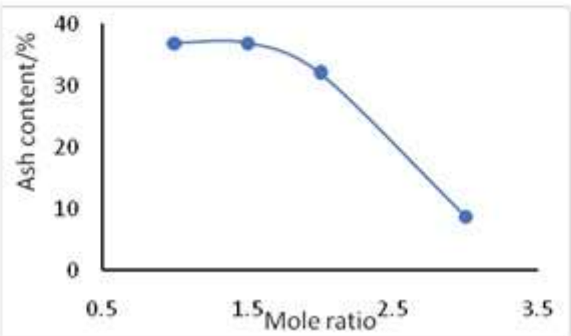


Figure 1: Effect of mole ratio of potassium carbonate/silica to ash content

Figure 2 shows the various extraction times of ash content with the ratio of potassium carbonate to 3:1 silica content. Extraction of silica through the reflux process with potassium carbonate solution produced charcoal with the lowest ash content of 4.34% with extraction time of 3 hours.The extraction of silica from rice husk charcoal with potassium carbonate solution was quite effective and the silica content was dependent on the quality of charcoal. The presence of silica can cause the clogging of the pores on charcoal and reduces its surface area. In addition, silica is an electrical insulator and can affect the carbon conductivity obtained.

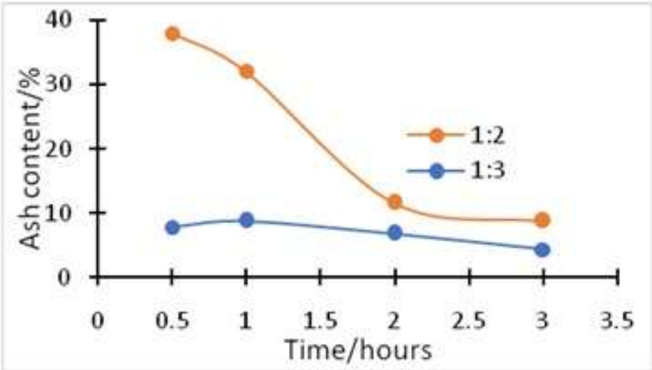


Figure 2: Effect of extraction time on ash content

The charcoal free of silica is then calcined at various temperatures (500, 700 and 900°C) for 2 hours in the atmosphere of argon gas. The calcination process is to increase the degree of carbonization because high temperatures are able to remove the volatile components in charcoal so as to increase the carbon content and increase the regularity of its structure. Regularity of the structure will affect the value of conductivity (electrical conductivity properties).

Figure 3 is a graph of the percentage of carbon obtained from varying the temperatures of the calcination process exposed to argon gas. The percentage of carbon decreases as the temperature of calcination increases, as more volatile substances were released from carbon rice husk and the fixed carbon content is increased.

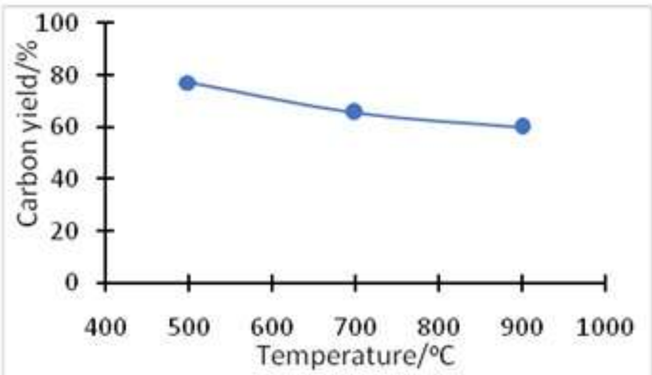


Figure 3: Effect of calcination temperature of carbon obtained in the calcination process

Fourier Transform Infrared Spectroscopy: To qualitatively characterize surface groups on carbons prepared from rice husk, FTIR (Fourier Transform Infrared

Spectroscopy) transmission spectra were collected for samples prepared in this study (Figure 4). A broad band located around 3400 cm^{-1} is typically attributed to hydroxyl groups or absorbed water. Carbons produced from rice husk can also be caused by silanol groups. The band around 1600 cm^{-1} is usually caused by the stretching vibration of C=O in ketones, aldehydes, lactones and carboxyl groups; the band around 11400-1500cm^{-1} is attributed to aromatic ring or C=C stretching vibration. This indicates the formation of carbonyl groups and the carbonization of the precursor.

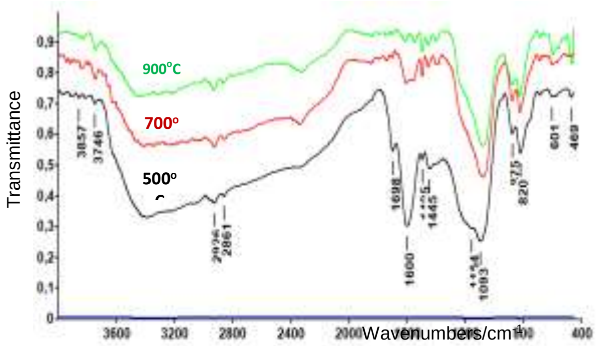
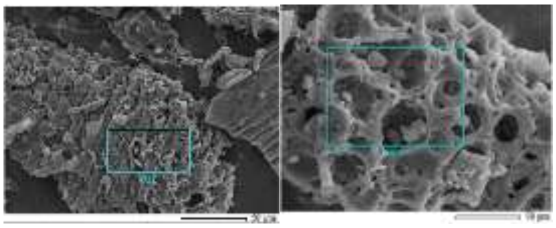


Figure 4: FTIR spectra of calcined carbon at a temperature of 500-900°C

The relative intensity of the band around 1600 cm^{-1} displayed decreases with the change of calcination temperature from 500 to 900°C. For temperature above 700°C, the relative intensity of the band at 1600 cm^{-1} began to disappear with the increase in activation temperature. The strong bands located around 1088cm^{-1} and 803cm^{-1} are attributed to asymmetric and symmetric stretching of the Si–O band. After the extraction of silica and calcination, the relative intensities of these two bands displayed an obvious decrease. This trend was consistent with the change in ash content, suggesting that the presence of these two bands was due to the existence of silica and carbon after the extraction.

SEM-EDS image: Figure 5 is a SEM-EDS image of rice husk after extracting silica with potassium carbonate and calcined at a temperature of 900°C. In the SEM image, the carbon produced had a large pore (macropore) spread evenly throughout the carbon. After dissolution of silica using potassium carbonate, the EDX results in carbon showed that the outer surface no longer contained silicon and oxygen content was very low 0.54% (fig. 6A). The silica on the outer surface of the charcoal has all dissolved and the carbon contained is carbon fixed (fixed carbon).

The presence of silica trapped in the pore of carbon (fig. 6B), caused the carbon to still contain silica. The silica present in the carbon is dissolved by the extraction but due to cooling during filtration the solubility decreased and created precipitated deposits on the carbon pores. Another element still in the carbon was potassium derived from its own husk or potassium carbonate solution in the silica extraction process.



	A		B
C	97,28%		96,65%
O	0,54%		1,78%
Si	0,00%		1,58%
K	1,82%		-

Figure 5: SEM-EDX image of carbon husk rice after extraction of silica with potassium carbonate

XRD: XRD analysis is used to investigate the structure of carbon produced. Figure 6 shows the XRD pattern on the initial carbon and carbon after extraction of silica with potassium carbonate by reflux method at various calcination temperatures. The diffractogram pattern on carbon after extraction with potassium carbonate had a wide peak at 2θ = 24.1° and at 43.9°. Higher calcination temperature shows the peak at 2θ = 43.9° higher, indicating that the higher carbon calcination temperature produced had caused the carbon to partially grafitized.

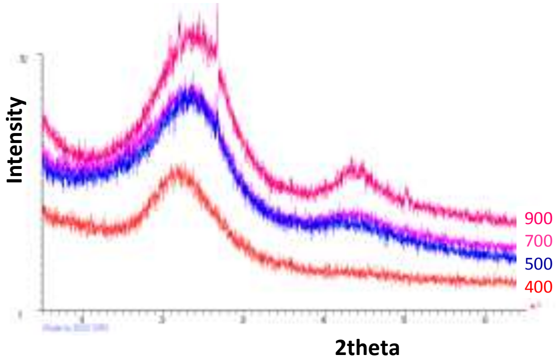


Figure 6: Diffractogram of rice husk char and carbon after silica extraction at temperature variations of calcination

Conclusion

The most effective silica extraction is using potassium carbonate solution with ratio of 1: 3 using the reflux method. The carbon obtained had an ash content of 4.34% and is amorphous.

Acknowledgement

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